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Highly efficient photocatalyst Bi_2MoO_6 induced by blue light-emitting diode

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ABSTRACT

The applicability of blue light-emitting diode (LED, λ = 465 nm) as the light source for environmental remediation by photocatalyst Bi_2MoO_6 was investigated. Two target compounds, phenol and ibuprofen (IBP), were selected as the model pollutants to evaluate the photocatalytic activities. The photocatalytic inactivation of *Escherichia coli* (*E. coli*) was also conducted to check the feasibility of using blue LED as the light source for the disinfection of bacteria. The results showed that efficient elimination of phenol and IBP and inactivation of *E. coli* were realized under a 3 W blue LED in the presence of Bi_2MoO_6. This demonstrates that LED is a competitive and promising alternative light source for the application in environmental remediation because the electrical energy consumption of LED decreased dramatically compared with other light source.

1. Introduction

One of the most urgent issues modern societies are faced with today is the deterioration of the environment [1,2]. A tremendous set of environmental problems related to water pollution, widespread harmful microorganisms and air contamination exist on a global scale [3–7]. For example, due to the wide applications, substantial quantities of phenolic compounds are dumped into the environment as industrial wastewater every year, which has emerged as an important environmental issue and constitutes the most important family of toxic non-biodegradable compounds [8]. Another class of hazardous contaminants that contributes partially to the environmental degradation is the pharmaceuticals residues [9,10]. Non-steroidal anti-inflammatory drugs (NSAIDs) are one group of the most consumed pharmaceuticals with more than 70 million annual prescriptions in the world [11]. Unfortunately, due to their growing use, NSAIDs have been found in increasing quantities in wastewater, surface water, and even in drinking water, which could bring about damages to the botany and fauna present in aquatic systems [12,13]. Harmful microorganisms are another hazards that threaten the public health and cause millions of deaths and cases of disease and disability every year [14]. Especially, intestinal parasitic infections and diarrheal diseases caused by bacterias have become pervasive problems afflicting people throughout the world [15–17].

In order to address this significant problem, extensive research is underway to develop advanced methods for the elimination of hazardous matters from the environment. Photocatalytic processes using semiconductor particles as photocatalysts under appropriate illumination regarding environmental applications are attracting extensive attention. Compared to conventional technologies, semiconductor-based heterogeneous photocatalysis has many advantages, including mild operating conditions, avoiding the use of hazardous chemicals, and complete oxidation of organic pollutants [18,19].

Photocatalytic processes require light illumination for the activation of photocatalysts. Thus the selection of the light source is crucial for photocatalysis because high energy consumption is a big obstacle for the practical application of a photocatalyst. High energy consumption originated from low quantum efficiency brings high cost. Recently, the development of visible light-emitting diodes (LED) makes it a potential candidate. The visible LED has been widely used in outdoors and indoors lightings, and they provide different lights of varying monochromatic wavelengths. Compared with conventional light sources, LED presents several merits. LED are far more efficient in converting electricity into light because the light emission by LED is induced by the recombination of excessive electrons and holes. Therefore, high quantum yields which are close to unity may be attained, resulting in low electricity consumption. Moreover, they have a long lifetime of more than 100,000 h and are much more rugged and compact than incandescent lamps [20]. Considering all such merits, the visible LED is expected to be a practical and competitive alternative light source for future photocatalysis applications.

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In order to harness the light emitted by visible LED, however, a visible-light-induced photocatalyst whose absorption edge is larger than the emission wavelength of the LED is needed. Fortunately, Bi_2MoO_6 with an absorption edge located at ca. 490–500 nm [21,22] is a potential candidate to meet these requirements. The wide absorption range enables Bi_2MoO_6 to work under the excitation of blue LED with main emission wavelength of 465 nm. Therefore, blue LED combined with the Bi_2MoO_6 photocatalyst is expected to have promising applications in environmental remediation. However, there are only a few studies about TiO_2 photocatalysis under UV-LED [23–27], and the Bi_2MoO_6 photocatalysis under blue LED was never reported.

In this study, the applicability of blue LED as the light source for environmental remediation, including the removal of two typical organic contaminants, phenol and ibuprofen (IBP), which belong to the phenolic compounds and pharmaceuticals, respectively, and inactivation of a pathogenic bacteria, *Escherichia coli* (*E. coli*), in the presence of Bi_2MoO_6 photocatalyst, was investigated for the first time. The obtained results indicated that efficient photocatalytic degradation of phenol and IBP and inactivation of *E. coli* were realized under a 3 W blue LED in the presence of Bi_2MoO_6. Moreover, it was found that LED is a much more energy-saving light source than Xe lamp, suggesting the feasible and potential use of LED as the light source for the application in environmental remediation.

2. Experimental

2.1. Preparation of photocatalysts

The Bi_2MoO_6 photocatalyst was prepared by a hydrothermal process. In a typical procedure, 2 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ and 1 mmol of $Na_2MoO_4{\cdot}2H_2O$ were dissolved in a 4 M nitric acid solution and deionized water, respectively. After that, these two solutions were mixed together and the pH value of the final suspension was adjusted to around 6 by the addition of a 2 M NaOH solution. Then the suspension was added into a 50 mL Teflon-lined autoclave up to 80% of the total volume. The autoclave was sealed in a stainless steel tank and heated at 160 °C for 12 h. Subsequently, the autoclave was cooled to room temperature naturally. The products were collected by filtration, washed with distilled water for several times, and then dried at 60 °C in air for 12 h.

2.2. Characterization

The phase and composition of the as-prepared sample were measured by X-ray diffraction (XRD) studies using an X-ray diffractometer with Cu Kα radiation under 40 kV and 100 mA and with the 2θ ranging from 20° to 70° (Rigaku, Japan). The morphologies and microstructures of the as-prepared sample were investigated by scanning electron microscopy (SEM, JEOL JSM-6700F). UV–vis diffuse reflectance spectra (DRS) of the sample were recorded with a UV–vis spectrophotometer (Hitachi U-3010) using $BaSO_4$ as reference.

2.3. Photocatalytic degradation test

Photocatalytic degradation of phenol and IBP by Bi_2MoO_6 photocatalyst was performed as follows: 50 mg of the photocatalyst was dispersed in a 50 mL solution of phenol (20 mg L^{-1}) or IBP (80 mg L^{-1}). Before illumination, the suspension was magnetically stirred in the dark for 1 h to ensure adsorption/desorption equilibrium of phenol or IBP with the photocatalyst powders, and then exposed to light from a 3 W blue LED (λ = 465 nm). After a certain period of irradiation, 3 mL suspension was sampled and centrifuged to remove the photocatalysts. The concentration variation of phenol was obtained according to the linear relation between the absorbance (at 269 nm) recorded using a Hitachi U-3010 UV–vis spectrophotometer.

IBP concentrations were monitored by a high-performance liquid chromatograph (HPLC, Agilent 1200) after sample-filtration with a Phenomenex reversed phase column (Zorbax SB RRHT C18, 2.1 mm × 50 mm inner diameter, 1.8 μm beads). A mobile phase of acetonitrile and acetic acid (0.25 M) in 75:25 proportion was employed. The flow rate was maintained at 1.0 mL min^{-1}. Total organic carbon (TOC) analysis was carried out with an elementar liqui TOC II analyzer in order to evaluate the mineralization degree during the experiment.

2.4. Photocatalytic bactericidal test

E. coli, a Gram-negative bacterium, was used as a model bacteria in this study. It was incubated in Lysogeny Broth (LB) medium at 37 °C for 18 h. Cells were harvested from overnight culture by centrifugation at 4000 rpm for 5 min and then washed twice with 0.9% saline.

The bactericidal activity was evaluated by the inactivation of *E. coli* under blue LED irradiation (λ = 465 nm). All materials used in the experiments were autoclaved at 121 °C for 40 min before use to ensure sterility. The treated cells were suspended and diluted to a cell suspension of ~2×10^7 cfu/mL with 0.9% saline to remove the influence of osmotic pressure on bacterial cells. The final photocatalyst concentration was adjusted to 0.5 mg/mL. The reaction mixture was stirred with a magnetic stirrer to prevent settling of the photocatalysts. The experiments were carried out at room temperature. Before and after the experiments, an aliquot of the reaction mixture was immediately diluted with 0.9% saline and plated on LB-agar plates. The colonies were counted after incubation at 37 °C for 24 h.

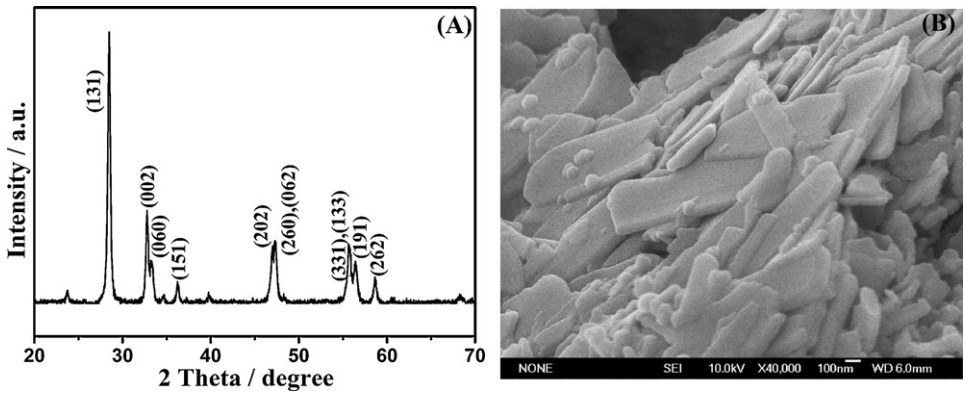

Fig. 1. (A) XRD patterns of the as-prepared product; (B) SEM image of the Bi_2MoO_6 sample.

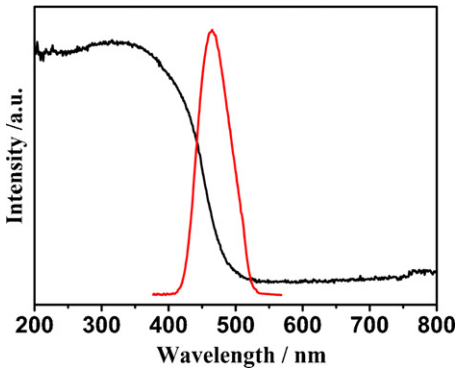

Fig. 2. Black line: UV–vis diffuse reflectance spectra of the Bi_2MoO_6 product. Red line: emission spectra of the blue LED. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

All of the above experiments were repeated three times and the average values were given.

3. Results and discussion

3.1. Crystal structure, morphology and optical properties of the product

The phase structure of the prepared product was investigated by powder X-ray diffractometer. The diffraction pattern in Fig. 1(A) shows that all the peaks can be indexed as orthorhombic Bi_2MoO_6 phase (JCPDS Card no. 77-1246) and no other peaks from possible impurities are detected. The SEM micrographs of the Bi_2MoO_6 sample shown in Fig. 1(B) indicated that the prepared Bi_2MoO_6 has a rectangular plate-like structure with a lateral size of several hundred nanometers.

Diffuse-reflectance spectroscopy (DRS) is an important method for characterizing the optical properties of semiconductor materials. The DRS spectrum of the as-prepared Bi_2MoO_6 sample is shown in Fig. 2. The sample exhibited an intense absorption in the visible-light range, which suggests the property of being photoactive under visible-light irradiation. The absorption edge of the Bi_2MoO_6 sample is located at ca. 500 nm. The emission spectra of the blue LED used in our case is also shown in Fig. 2. It is obvious that the main emission wavelength of the blue LED (465 nm) is within the absorption range of Bi_2MoO_6. Therefore, it can be expected that the prepared Bi_2MoO_6 has a good photocatalytic potential under the blue LED irradiation.

3.2. Photocatalytic degradation of phenol

As one of the most abundant pollutants in industrial wastewater, phenol has attracted much attention in the last two decades due to its high toxicity and the frequency of industrial processes producing water contaminated by phenol. Moreover, phenol serves as intermediates in the industrial synthesis of products and its presence contributes notably to the pollution of the effluents, thus it is usually taken as a model compound for wastewater treatments. To demonstrate the applicability of blue LED as a potential excitation light source, the photocatalytic degradation of phenol under a 3 W blue LED was conducted and compared with that of under a 500 W Xe lamp ($\lambda > 420$ nm). The degradation efficiency of phenol versus the reaction time under the Xe lamp was demonstrated in Fig. 3(A). The blank test in the absence of Bi_2MoO_6 showed that the photolysis of phenol under the Xe lamp was negligible. In contrast, in the presence of Bi_2MoO_6, phenol was completely degraded after 3 h of irradiation. Under the illumination of a blue LED, the photolysis of phenol could not be realized either, while complete degradation of phenol was reached after 8 h of irradiation in the presence of Bi_2MoO_6 photocatalyst (Fig. 3(B)).

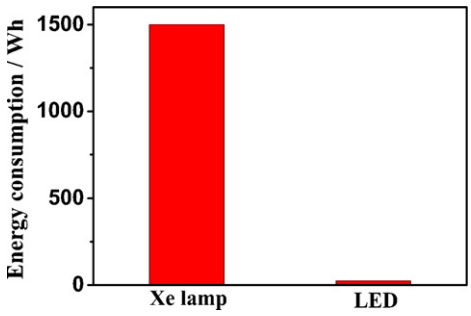

Fig. 4. Comparison of electrical energy consumption by LED and Xe lamp.

In view of future applications of photocatalysis, we hope to decrease the energy consumption to the largest extent, so the choice of the light source is very important. Rapid advancement of LED development has opened the possibility of employing LED as an alternative artificial light source. To reach the complete degradation of phenol, the electrical energy consumption of Xe lamp and blue LED were 1500 Wh and 24 Wh, respectively, as shown in Fig. 4. In other words, the electrical energy consumption of Xe lamp was 62.5 times that of blue LED. From this point of view, LED is no doubt a much superior activation light source to Xe lamp.

3.3. Photocatalytic degradation of IBP

The compound 2-[3-(2-methylpropyl) phenyl] propanoic acid, commercially available as IBP, is an anti-inflammatory and antipyretic drug widely used against musculature pain and inflammatory disorders, whose presence in water could bring about harmful toxicological consequences in aquatic environment.

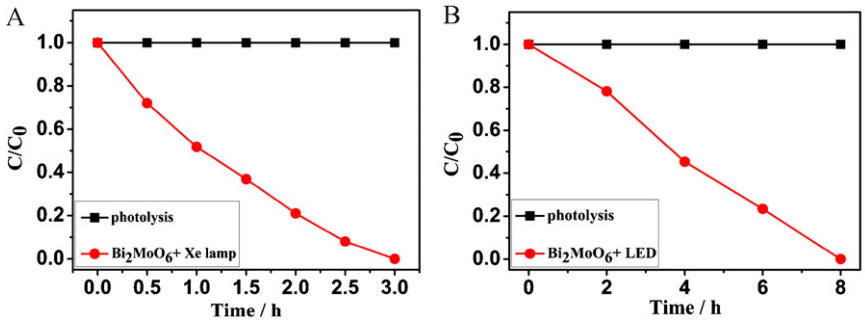

Fig. 3. (A) Photocatalytic degradation of phenol under a 500 W Xe lamp ($\lambda > 420$ nm) by the as-prepared Bi_2MoO_6 product; (B) photocatalytic degradation of phenol under a 3 W blue LED ($\lambda = 465$ nm) by the as-prepared Bi_2MoO_6 product.

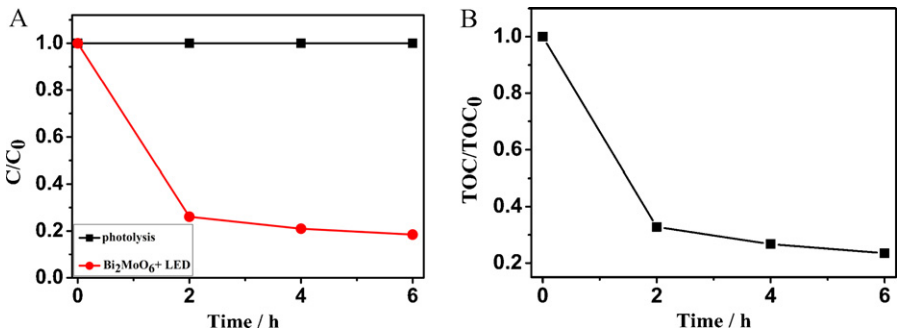

Fig. 5. (A) Degradation efficiency of IBP as a function of time in the presence of Bi_2MoO_6 under blue LED irradiation; (B) TOC removal efficiency of IBP as a function of time in the presence of Bi_2MoO_6 under blue LED irradiation.

Therefore, the treatment of these wastewater is important before discharging them into the ecosystem.

In most of previous works, photocatalytic degradation of IBP was conducted using the wide band-gap semiconductor TiO_2 as the catalyst, and the UV light was employed as the light source [28–30]. To the best of our knowledge, this is the first time that blue LED was exploited as the light source to eliminate IBP. The result shown in Fig. 5(A) confirmed that IBP can be effectively degraded by Bi_2MoO_6 photocatalyst under blue LED irradiation. After 6 h of irradiation, the degradation rate of IBP reached 81.5%, while no degradation of IBP was attained by photolysis in the absence of Bi_2MoO_6. This was not unexpected, due to the low IBP molar absorption coefficient above 300 nm.

It has been widely reported that some of the intermediate products of a degradation process are more toxic and carcinogenic than the parent organic compounds [31,32]. Hence, the complete degradation of the pollutants should be ensured before discharging them into the ecosystem. Therefore, TOC, which has been widely used to evaluate the degree of mineralization of organic species, was measured in the photodegradation process of IBP by the as-prepared Bi_2MoO_6 under blue LED, as shown in Fig. 5(B). The results showed that the TOC value decreased steadily with the irradiation time and the TOC removal efficiency in the presence of Bi_2MoO_6 reaches a value of 76.5% after 6 h of irradiation, indicating that IBP could be mineralized by Bi_2MoO_6 photocatalyst under blue LED.

3.4. Bacterial inactivation under blue LED irradiation

In order to evaluate the feasibility of the application of blue LED as the light source used for the disinfection of bacteria, the photocatalytic disinfection ability of *E. coli* by the Bi_2MoO_6 photocatalyst under blue LED irradiation was studied. The antibacterial activity of the Bi_2MoO_6 photocatalyst was exhibited by the killing effect of *E. coli*, which was evaluated through the decrease of the colony number formed on an agar plate. According to Fig. 6, *E. coli* can be almost completely inactivated within 6 h with Bi_2MoO_6 photocatalysts under blue LED irradiation. Blank test without photocatalyst showed that the colony number of bacteria decreased at a low level after blue LED illumination, whereas the colony number of bacteria was almost the same with Bi_2MoO_6 photocatalyst in the dark, indicating that the photocatalyst itself is not toxic to *E. coli*. The *E. coli* survival ratios under variant conditions shown in Fig. 7 demonstrated that *E. coli* inactivation efficiency is up to 95.3% after 6 h of blue LED illumination in the presence of Bi_2MoO_6, while neither blue LED irradiation without the photocatalyst nor Bi_2MoO_6 in the dark showed much bactericidal effects on *E. coli*, indicating that the bactericidal effect on *E. coli* is surely ascribed to the photocatalytic

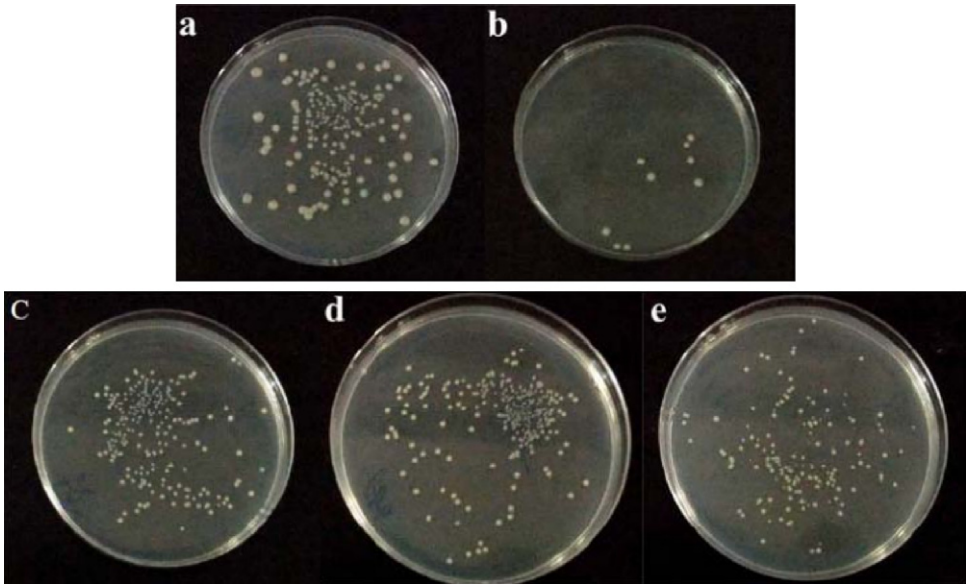

Fig. 6. Images of colonies on Petri dishes cultured with *E. coli* in 0.9% saline water dispersions: (a) *E. coli* suspension before reaction; (b) *E. coli* suspension containing 0.5 mg/mL Bi_2MoO_6 under the irradiation of blue LED for 6 h; (c) *E. coli* suspension before reaction; (d) *E. coli* suspension containing 0.5 mg/mL Bi_2MoO_6 in the dark; (e) *E. coli* suspension without Bi_2MoO_6 under the irradiation of blue LED for 6 h.

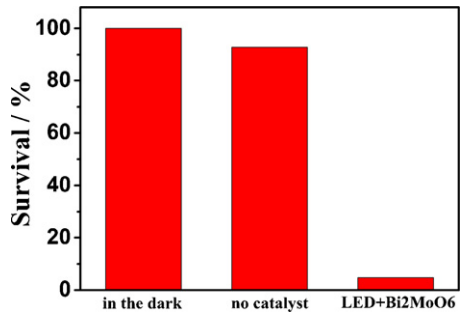

Fig. 7. Survival ratio of *E. coli* ($\sim 2 \times 10^7$ cfu/mL, 20 mL) in aqueous dispersions.

reaction of the Bi_2MoO_6 under blue LED irradiation. Therefore, blue LED induced photocatalysis by Bi_2MoO_6 photocatalyst has excellent applications not only in the elimination of organic pollutants but also in the disinfection of bacteria.

4. Conclusion

In summary, this study explored the feasibility of the application of blue LED as the light source for environmental remediation. Efficient removal of phenol and IBP and inactivation of *E. coli* were realized in the presence of Bi_2MoO_6. Moreover, the electrical energy consumption of LED decreased significantly compared with that of the generally used Xe lamp. Therefore, LED represents a promising and competitive alternative light source for photocatalysis applications which possess a wide range of applied potential in the field of environmental remediation, such as antibacterial, water treatment, air purification, etc.

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